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ORGANIC SUBSTITUTES FOR CHARCOAL IN
"BLACK POWDER" TYPE PYROTECHNIC
FORMULATIONS

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20. Abstract (Cont'd):

and phthalein salts all produced pyrotechnics which sustained combustion and some even burned faster than charcoal-black powder. It was also found that the phenolics which contained catechol/hydroquinone moieties (good organic reducing agents) were less reactive than other phenolics. This effect has been attributed to a deactivating reaction between sulfur and the catechol/hydroquinone effect.

One of the mixtures, that containing phenolphthalein, was evaluated further by determining strand-burn rates at various nitrogen pressures to one hundred atmospheres. Combustion rates and photographed features parallel those of black powder.

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INTRODUCTION AND BACKGROUND

Black powder is a mixture of 75 percent potassium nitrate, 10 percent sulfur, and 15 percent charcoal. It is probably the oldest known energetic material and has been used throughout the world for centuries. Even though black powder has been in use for years, the factors that control its combustion properties are not known and certainly not well understood. The reasons for this ambiguity are related to the nature of the composition as it is a heterogenous mixture of three solids, pressed to about 95 percent theoretical maximum density. Also, charcoal in black powder is a naturally derived substance which contains up to 35 percent tar-like constituents and varies from one source to another. Such variance has been found to have a great impact on the combustion properties of black powder.¹

Recently poor combustion properties of one lot of black powder has been cited as a cause for weapon malfunctions.² One problem area of prime concern is that various lots of black powder made by a particular manufacturer and black powder made by various manufacturers, using apparently equivalent processes, produce a pyrotechnic with different combustion characteristics. In fact, it has been possible to identify "good" and "bad" lots, in relation to device performance, without a clear understanding as to the particular differences involved.³ Such variances are believed to be due to the varying chemical and physical properties of charcoal and to the physical properties of black powder.

The reasons for the difficulties in characterizing charcoal used in black powder are many. It is an amorphous substance; it reacts and changes on heating; it is a mixture of many components; and only small portions of it dissolve in solvents. Since the material cannot easily be characterized, it has been impossible to learn what reactions might be important in combustion. One hope embraced in this work was to determine if a pure organic compound could be identified that would be an adequate substitute for charcoal and render the same performance, in a reproducible manner, as does "good" black powder. Such a substitute should lead to a more easily studied system to model the combustion processes of black powder. An added benefit may be a new type of pyrotechnic material in which a non-varying chemistry of combustion could exist and uniform physical properties could be maintained.

¹James E. Rose, "Investigation on Black Powder and Charcoal," IHTR 433, September 1975, Naval Ordnance Station, Indian Head, MD.

²K. J. White, H. E. Holmes, and J. R. Kelso, "Effect of Black Powder Combustion on High and Low Pressure Igniter Systems," Proc. of the 16th JANNAF Combustion Meeting, CPIA Publication 308, Vol. 1, pp. 477-497, December 1979.

³K. J. White, and R. A. Sasse', "Some Combustion and Flamespread Characteristics of Black Powder," Proc. of the 18th JANNAF Combustion Meeting, CPIA Publication 347, Vol. 2, p. 253, October 1981.

In choosing organic compounds as substitutes for charcoal in black powder, it is necessary to make an assumption about the important functionality that may contribute to combustion. Since the oxidation of charcoal in combustion is an electron transfer process, it follows that charcoal's combustion should be made more rapid by functional groups which make electron transfer easier or by easily oxidizable groups present in the material. This hypothesis suggests two classes of model compounds that should be evaluated to study the reactivity of charcoal in black powder: polynuclear aromatics and organic reducing agents.

In the first class of model compounds, we will determine if electrons delocalized over large aromatic pi systems facilitate electron transfer and therefore oxidation. If this is important, then polynuclear aromatic compounds, when substituted for charcoal in black powder, should support combustion.

The second class of compounds studied probes a hypothetical role for the volatiles in charcoal during combustion. Rose observed that the "volatiles" in the charcoal play a crucial role in combustion,^{1,4} and fine papers relating volatiles to burning rate were also offered by Hintze⁵ and by Kirshenbaum.⁶ Gray, March, and Robertson⁷ related volatile content to roasting temperature and Sasse⁸ presented complete analysis of charcoal used to make black powder. Although the subject of volatiles appears to be well presented, the mechanisms of combustion are not understood. It is well known that charcoal is not just carbon; it contains 5 to 20 percent (by weight) oxygen, up to 5 percent hydrogen, and smaller amounts of other elements. We suspected that a significant amount of oxygen might be present in the charcoal as catechol or hydroquinone moieties. These compounds are very good organic reducing agents and can easily undergo two-electron oxidations to quinones. In addition, the catechol structure is known to occur in lignin which accounts for approximately 20 to 30 percent of the weight of wood before pyrolysis.⁹

⁴James E. Rose, "Black Powder - A Modern Commentary," *Proceedings of the 10th Symposium on Explosives and Pyrotechnics*, 6A-1, 1979, Franklin Research Institute, Philadelphia, PA.

⁵W. Hintze, *Explosivstoffe*, Vol. 2, p. 41, 1968.

⁶A. D. Kirshenbaum, *J. Ballistics*, p. 171, July 1978.

⁷E. Gray, H. March, and J. Robertson, "The Influence of Charcoal in the Combustion of Black Powder," *RARDE*, Fort Halstead, Seven Oaks, England. Presented at Basic and Applied Pyrotechnics International Conference, Arcachon, France, October 1982.

⁸R. Sasse', "Characterization of Maple Charcoal Used to Make Black Powder," *ARBRL-MR-Q3322 Ballistic Research Laboratory, USA ARRADCOM, Aberdeen Proving Ground, MD*, November 1983. (AD-A136-513)

⁹E. Ott, H. M. Spurlin, and M. W. Grafflin, *High Polymers, Vol. 5, Cellulose and Cellulose Derivatives* Part II, p. 514, Interscience Publishers Inc., New York, 1954.

The conditions for the pyrolysis of wood required to make a good black-powder charcoal are stringent but not severe. Thermal analysis has shown that significant amounts of lignin remain in charcoal used for black powder^{7,8} and extreme pyrolysis, to 900C in an inert atmosphere, destroys these organics resulting in a weight loss. Therefore, it is proposed that the lignins originally present act as reducing agents in black powder making charcoal's combustion more facile. To probe the importance of this type of reaction in combustion then, a large number of polyphenolic compounds were evaluated as substitute compounds for charcoal. Some of these were capable of a facile two-electron oxidation and others were not.

Another factor considered in choosing the organic substitutes for charcoal was melting point. Effort was made to choose high-melting materials of the types described above. It was felt that a low-melting-point material would liquify and agglomerate prior to reacting. This would prevent good mixing of the three components which is required for combustion. The compounds selected are listed in Table 1 showing chemical structure, chemical composition, and melting point.

EXPERIMENTAL

Characterization of pyrotechnic mixtures was done by Differential Scanning Calorimetry (DSC), and combustion-rate studies of pressed sticks were conducted at one atmosphere. While these two methods by no means constitute complete characterization, they did permit us to screen a large number of materials; and it was hoped these tests would be adequate to identify some of the functionality required for reaction and combustion. Better characterization will require a more extensive study. One of the mixtures was evaluated further by determining strand-burn rates at various pressures of nitrogen.

A. Preparation of Pyrotechnic Mixtures

The pyrotechnic powders were made by grinding a mixture of 75 parts of potassium nitrate, 10 parts sulfur, and 15 parts of a crystalline organic fuel (by weight) in a mortar and pestle until they passed through a 120-mesh screen.¹⁰ These proportions are used in black powder and no further attempt was made to optimize the stoichiometry. The Maple charcoal used was supplied by Roseville Charcoal Co. of Zanesville, OH; and this material was used by the Army Ammunition Plant in Charlestown, IN.⁸ Such mixtures were compared to charcoal-black powder which was prepared in the same manner and used as a control in these experiments. Had the samples been ground finer as is done in a jet-mill, they would have burned twice as fast. In an effort to explore the importance of the nitrate oxidizer's melting point, a low melting eutectic of 70 percent potassium nitrate and 30 percent sodium nitrate was prepared, ground, and used in place of the pure potassium nitrate in one experiment. It had a melting point near 240°C.

¹⁰R. Sasse', "Strand Burning Rates of Black Powder to One Hundred Atmospheres," *Proc. of the 19th JANNAF Combustion Meeting, CPIA Publication 366, Vol. 1, p. 13, October 1982. (AD-A129-087)*

B. Strand-Burning Experiments

The pyrotechnic material was formed into rectangular parallelepipeds by pressing a weighed sample (0.8g) in a constant-volume die where a spacer limited piston travel and controlled dimensions. Internal free volume was kept small; e.g., free volume in the fluorescein sample was 5.1 percent. Some samples were inhibited with a coat of cyanoacrylate-based glue. The difference in burn rate between an inhibited and non-inhibited sample is near two.

Many different types of samples were burned at one atmosphere and combustion was recorded on video tape. Burning times were measured by counting picture frames (see Table 2). In most cases, only one sample was prepared of each mixture; therefore, the burning rates are approximate and should be examined with caution. Determination of exact burning rates will require a more extensive study.

For one pyrotechnic mixture, containing phenolphthalein, strand-burn rates were measured at various high pressures of nitrogen. Cinematography, at 1000 frames per second, was used to record combustion; and burning rates were determined from the slope of the line describing the position history of the regressive surface. This technique and high pressure cell have been described.¹⁰ The samples had a density of 1.86; theoretical maximum density is 1.93.

C. Thermal Analysis

Differential Scanning Calorimetry was performed on a Dupont 990 Thermal Analyzer equipped with a high-pressure DSC cell base. Samples were analysed as follows: approximately 10 mg of loose pyrotechnic powder was placed in an aluminum sample pan which was covered with a perforated aluminum lid. This was placed in the DSC, flushed with argon and then heated at a rate of 20° C/min. from ambient to 500°C. The phase changes for potassium nitrate, sulfur, and organic compounds were noted; but they are not included in Table 3. The first temperature is the onset value; the second is the peak temperature.

RESULTS AND DISCUSSION

A. Polynuclear Aromatics

The first group of compounds studied were the polynuclear aromatic materials to determine if delocalizing electrons over a large aromatic pi system could facilitate electron transfer and enhance combustion. Pyrotechnic powders were made with anthracene, tetracene, p-quaterphenyl and rubrene in place of charcoal. None of these mixtures sustained combustion (Table 2). DSC analysis revealed a moderate to weak exothermic reaction normally observed between potassium nitrate and sulfur and no strongly exothermic reactions were observed below 500°C (Table 3).

It might be postulated that none of these materials would be good models for they do not have as extensive a fused aromatic system as does charcoal.

Graphite, however, has an even more extensive aromatic system than does charcoal and it too does not sustain combustion when used in a pyrotechnic mixture. We believe these results eliminate the possibility that the delocalization of electrons over large fused aromatic systems is a sufficient condition for the facile oxidation of charcoal in black powder.

B. Phenolic Compounds

The second class of compounds studied were phenolics which were further subdivided into two groups; the hydroquinone/catechol type compounds capable of undergoing a two-electron oxidation (quinizarin, leucoquinizarin, hydroquinone, and catechol) and other phenolics which are not (anthraflavic acid, fluorescein, phenolphthalein, and phenolphthalin). If the two-electron oxidation of the hydroquinone/catechol moiety plays an important role in combustion, then the former group of compounds should burn very well and the latter group should not.

These materials were incorporated into pyrotechnic powders and burned in pressed stick form; the results were surprising. All compounds which easily undergo a two-electron oxidation burned but they burned quite slowly. On the other hand, the polyphenolic compounds which could not undergo this hydroquinone to quinone type oxidation, burned very rapidly. In fact the latter group burned faster than the charcoal-black powder control (See Table 2). The most striking example of this is the comparison of the anthraflavic acid and quinizarin pyrotechnic powders. These two compounds are isomers; quinizarin is 1,4-dihydroxyanthraquinone and anthraflavic acid is 2,6-dihydroxyanthraquinone. The former compound burned at 0.08 cm/sec while the latter burned at 0.44 to 1.4 cm/sec. It is uncertain what is happening in these instances but the DSC data coupled with the combustion of the diketone-aromatic, anthraquinone, provides some insight.

The DSC analysis of the pyrotechnic powders containing organic compounds with catechol or hydroquinone moieties looked similar to those of charcoal-black powder. With black powder there is a double-peaked exotherm associated with the melting point of the potassium nitrate. This peak has been labeled the preignition exotherm and has been attributed to a reaction involving all three components in black powder. In the compositions containing catechol or hydroquinone moieties, this peak is present; and the magnitude of the reaction is similar to that observed in black powder. The next peak in the DSC's of these materials has been labeled the "ignition" exotherm because it is during this second exotherm that the greatest amount of heat is released. With black powder this peak is very strong and occurs at about 425°C.

In the catechol/hydroquinone powders, the "ignition" peak is reduced in magnitude or it occurs at temperatures in excess of 450°C. It appears that these easily-oxidized systems are being oxidized to materials that are much less reactive towards subsequent oxidation. This supposition is supported by the inability of an anthraquinone pyrotechnic powder to sustain combustion. (Anthraquinone is the oxidized form of a hydroquinone, dihydroxyanthraquinone.)

Interestingly, the polyphenolic materials which could not undergo an easy two electron oxidation, such as the anthraflavic acid and the phthaleins, showed little or no exothermic reaction as the potassium nitrate melted; the

only reaction observed on the DSC trace was the "ignition" exotherm at about 425°C. Recall that these materials all burned well in their pyrotechnic mixtures. The question one must ask is, "How are these data reconciled with the proposed mechanism describing the role of charcoal's volatiles in the combustion of black powder?" Suggested mechanisms, which include charcoal-sulfur reactions, will be discussed.

C. Sulfur Reactions

In their paper on the thermal decomposition of black powder, Blackwood and Bowden¹¹ discuss the preignition reaction between potassium nitrate, sulfur, and charcoal. They felt that preignition occurred in several steps where the first step is a nonexothermic reduction of sulfur by the organics in charcoal:



This is followed by an exothermic reaction between potassium nitrate and "reduced" sulfur. It may be possible that the species that "oxidizes" the catechol/hydroquinone moieties to some nonreactive compound is the sulfur and not the potassium nitrate. If this is the case, then a sulfurless pyrotechnic powder made with a hydroquinone derivative should burn much better than the equivalent pyrotechnic powder with sulfur. To evaluate this hypothesis, sulfurless powders were made with quinizarin (which contains a hydroquinone moiety) and anthraflavic acid (which does not contain a hydroquinone moiety). Both of these powders burned very rapidly. For the quinizarin this is an increase in rate by a factor of 5-10 and for the anthraflavic acid, little change is observed. It appears then that sulfur is the reactant which turns the hydroquinone/catechol moieties into a less reactive species. The DSC results of the sulfurless compositions support the hypothesis that sulfur is the deactivating species for catechol and hydroquinone systems. When sulfur is not present, these mixtures exhibit stronger ignition exotherms at lower temperatures (see Table 3). Decreases in ignition temperature were 428 to 442°C for quinalizarin, 465 to 430°C for leucoquinizarin, and 475 to 397°C for quinizarin. Other polyphenols exhibited the opposite trend but at a lower magnitude. It seems reasonable that the preignition reactions in charcoal-black powders could be due to a reduction of sulfur by catechol moieties originally present in the wood's lignin.

While reduction of sulfur by an organic does not seem to play a crucial role in the burn rate of black powder, perhaps it does play a role in the flame-spread rate of loose granular black powder grains. During the preignition reaction, highly flammable H₂S or organic sulfides⁶ might be released into the local atmosphere surrounding the powder.* Subsequent

¹¹J. D. Blackwood and F. P. Bowden, *Proc. Roy. Soc., London*, A 213, 285, 1952.

*DSC black powder data show no preignition exotherm when the analysis is performed in an open pan. This supports the hypothesis that gaseous compounds could be involved in the reaction.

ignition of these gases would accelerate the flame-spread rate. This hypothesis will have to be examined carefully both with charcoal-black powder and the model systems.

D. Other Compounds Studied

The discussion in the preceding paragraphs describes what may be occurring in the preignition exotherm of black powder but DSC and combustion data of other pyrotechnic powders reveal that many types of functional groups can cause this reaction. Powders made with terephthalic acid and the sodium salts of fluorescein and phenolphthalein showed similar preignition exotherms and these materials burned quite rapidly in strand-burning tests. No explanation is offered as to what might be occurring in these cases except to say there are probably alternative explanations for the preignition exotherm. These examples illustrate the very complex chemistry that is involved in any potassium nitrate/sulfur/organic system. The discussion also illustrates the magnitude of the black powder chemistry problem where the "organic" is a very poorly defined material, charcoal.

E. Physical States and Reactivity

A final point should be made concerning the influences of phase changes in relation to reaction. In black powder, exothermic reactions are first observed on melting of the potassium nitrate. In this study, it has been observed that all three components must first melt before exothermic reaction takes place as one might expect. However, in many cases, much higher temperatures were needed before any appreciable reactions were observed with DSC data. This was illustrated by using a low melting point eutectic of potassium nitrate and sodium nitrate in one of the pyrotechnic compositions. It was found that phenolphthalein, sulfur, and the nitrate salts would not react to produce an exotherm at 300°C and the melt had to be heated to over 350 degrees C before the onset of exothermic decomposition was detected. This experiment shows that melting of the components is not a sufficient condition for reaction to take place.

F. Strand-Burn Rates at High Pressure

Strand-burn rates for the system phenolphthalein /KNO₃/S as a function of nitrogen pressure are given in Figure 1. The figure also contains similar data for laboratory prepared black powder made from meal ground in a jet-mill. Had the phenolphthalein mixture been ground in a jet-mill one would expect it to burn twice as fast. This relationship becomes clearer when comparing the two systems that were hand ground having a particle size of 120 microns. Then the one atmosphere burn rates were nearly equal where the black powder had a burn rate of 0.58 cm/sec and the phenolphthalein mixture had a burn rate of 0.42 and 0.48 cm/sec. In contrast, finely ground black powder has a burn rate of 1.0 cm/sec.

The phenolphthalein system has similar burn rates to black powder and the burn-rate curves appear of similar shape. One important characteristic is that both systems exhibit a sharp change or "break" in curvature at a few atmospheres pressure. One is tempted to ascribe this commonality to high temperature equilibria or to chemical reactions of potassium nitrate, the common element in both systems. Another supporting argument is that black

powder reacts above the melting point of potassium nitrate and thus, the system is a liquid-solid reaction; in contrast, the phenolphthalein system reacts above the melting point of all constituents and is a liquid-liquid reaction. Therefore, the break cannot be due to the physical state of the fuel. However, at these temperatures some of the organics may undergo pyrolysis to carbon making the two systems alike. The only firm conclusion is that two pyrotechnic systems have similar breaks in their burning-rate curves.

From the cinematography the burning phenolphthalein "sticks" showed a liquid surface that was in extreme turbulence and liquid drops were propelled by the gas stream. No deconsolidation nor evidence of porous burning was observed and the inhibited "stick" burned in "cigarette fashion." The scenes were very similar to those of black powder, except the drops and liquid film appeared slightly larger.

CONCLUSIONS

The work described in this paper has shown that a variety of functionalized aromatic compounds, such as phenols, acids, and their salts, can support combustion in black powder type pyrotechnic formulations. Since so many types of compounds support combustion, it is impossible to say what functionality is really important in charcoal's combustion. Perhaps the variety of compounds that worked may explain why so many types of charcoal can function adequately in black powder. The negative results with the unfunctionalized polynuclear aromatics, however, do allow one to conclude that some sort of functionality must be present in the charcoal for rapid combustion to take place. This underscores the need to learn more about the chemical composition of charcoal. The studies done with the phenolic materials, in particular the hydroquinone/catechol systems, shows the profound effect sulfur can have on combustion. This has led to a hypothetical mechanism explaining sulfur's role in flame spreading which should be explored in future work.

From cinematography and burning-rate curve of the phenolphthalein pyrotechnic, it was shown that this system reacts as well as black powder and has similar physical combustion characteristics to black powder.

A practical outgrowth of this work is the potential that some of these organic substrates might prove to be acceptable substitutes for charcoal in black powder. A synthetic black powder ought to have much more reproducible and uniform combustion characteristics. It is realized that such pyrotechnic mixtures must be extensively tested before they can be seriously considered. Safety tests including drop weight, card gap, friction, and electrostatic sensitivity must be performed.

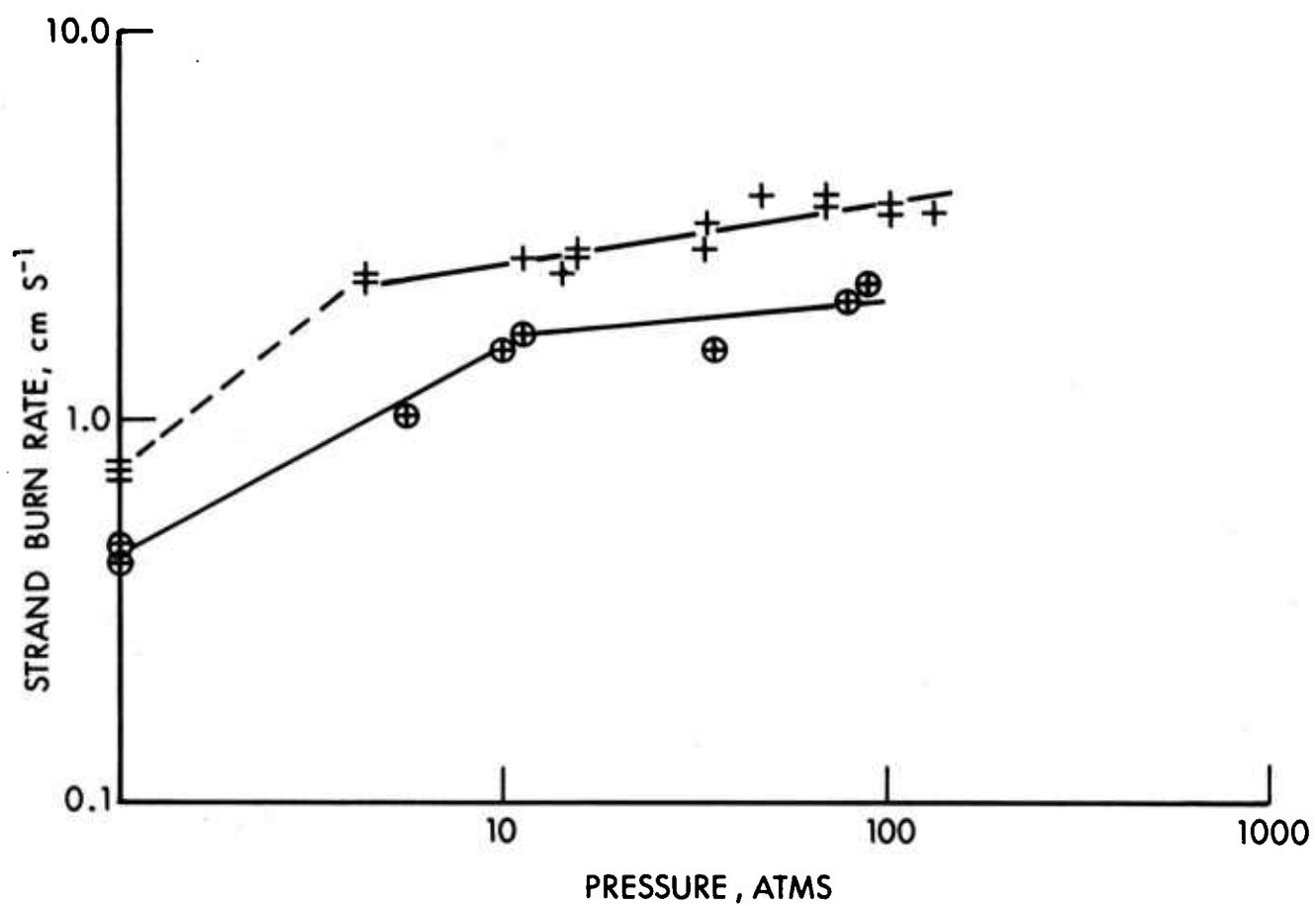


Figure 1. Strand-Burn Rate of Black Powder, +, and Phenolphthalein Pyrotechnic, ⊕.

TABLE 1. ORGANIC FUELS USED IN PYROTECHNIC POWDERS



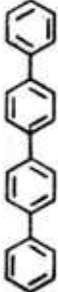
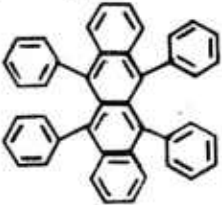
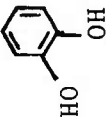

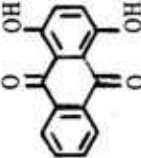
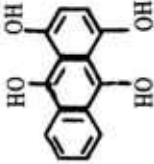
Compound	Structure	M.P.	%C	%H	%O	Other Elements
<u>Polynuclear Aromatic Compounds</u>						
Anthracene		218	94.31	5.66	---	---
Tetracene		300	94.70	5.30	---	---
p-Quaterphenyl		300	94.10	5.90	---	---
Rubrene		315	94.71	5.29	---	---
<u>Compounds Containing Hydroquinone and Catechol Moieties</u>						
Catechol		104	65.44	5.49	29.06	---
Hydroquinone		170	65.44	5.49	29.06	---
Quinizarin		200	70.00	3.36	26.64	---
Leucoquinizarin		146	69.41	4.16	26.42	---

TABLE 1. ORGANIC FUELS USED IN PYROTECHNIC POWDERS (CONTINUED)

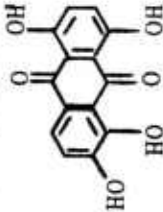
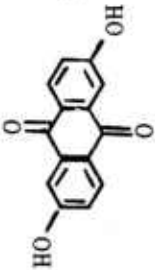
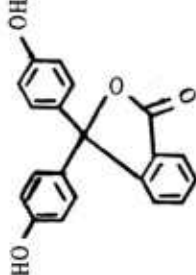
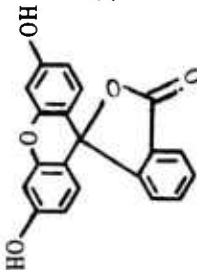
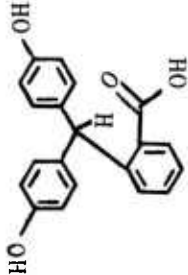
<u>Compound</u>	<u>Structure</u>	<u>M.P.</u>	<u>%C</u>	<u>%H</u>	<u>%O</u>	<u>Other Elements</u>
Quinalizarin		305	61.77	2.96	35.27	---
<u>Other Phenoxy Compounds</u>						
Anthraflavic Acid		360	70.00	3.36	26.64	---
Phenolphthalein		258	75.46	4.43	20.10	---
Fluorescein		314	72.28	3.64	24.07	---
Phenolphthalin		237	74.99	5.04	19.98	---

TABLE 1. ORGANIC FUELS USED IN PYROTECHNIC POWDERS (CONTINUED)

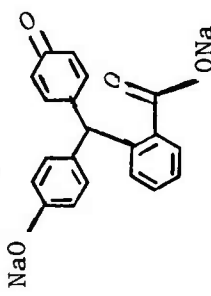
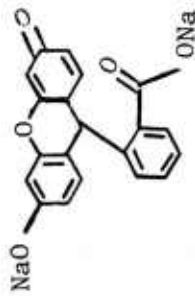
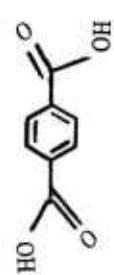
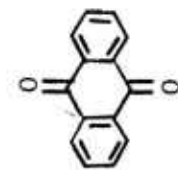

<u>Compound</u>	<u>Structure</u>	<u>M.P.</u>	<u>%C</u>	<u>%H</u>	<u>%O</u>	<u>Other Elements</u>
Phenolphthalein- Disodium Salt		---	66.30	3.34	17.67	Na, 12.70
Fluorescein- Disodium Salt		---	63.84	2.68	21.26	Na, 12.22
Terephthalic Acid (sub.)		300	57.83	3.64	38.52	---
Anthraquinone		286	80.76	3.87	15.37	---
Maple Charcoal (Ref.8)		---	80.95	2.94	12.66	Ash 3.15

TABLE 2. STRAND BURNING RATES OF PYROTECHNIC FORMULATIONS AT ONE ATMOSPHERE

<u>Compound</u>	<u>Melting Point, °C</u>	<u>Burn Rate** Without Sulfur, cm/s</u>	<u>Burn Rate* With Sulfur cm/s</u>
<u>Charcoal Black Powder</u>			
Maple Charcoal	---	---	.58
<u>Polynuclear Aromatics</u>			
Anthracene	218	---	NI
Tetracene	300	---	NI
p-Quaterphenyl	300	---	NI
Rubrene	315	---	NI
Graphite	---	---	NI
<u>Compounds Containing Hydroquinone and Catechol Moieties</u>			
Hydroquinone	170	NI	.13 ^a
Catechol	104	.54	slow
Quinizarin	200	.53 1.0 ^a	.08 ^a
Leucoquinizarin	146	.12	.05 ^a
Quinalizarin	305	.83	.15 ^a
Anthraquinone	286	---	NI

TABLE 2. STRAND BURNING RATES OF PYROTECHNIC FORMULATIONS AT ONE ATMOSPHERE (CONTINUED)

<u>Compound</u>	<u>Melting Point, °C</u>	<u>Burn Rate** Without Sulfur, cm/s</u>	<u>Burn Rate* With Sulfur cm/s</u>
<u>Other Phenolic Compounds</u>			
Anthraflavic Acid	360	.64 1.00 ^a	.44 1.43 ^a
Phenolphthalein	258	.59	.93
Fluorescein	314	.36	.62
Phenolphthalin	237	.57	.53 1.13 ^a
<u>Other Compounds</u>			
Phenolphthalein Disodium Salt	---	.62	.44 .85 ^a
Fluorescein Disodium Salt	---	---	.41 1.16 ^a
Terephthalic Acid	300	NI	.23 .33 ^a

* 75% KNO₃, 10% S and 15% organic by weight** 75% KNO₃ and 25% organic by weight

a Non-inhibited

NI No ignition

TABLE 3. DSC RESULTS OF PYROTECHNIC MIXTURES

System	Low Temperature Exotherm	Moderate Temperature Exotherm	High Temperature Exotherm	Comments
$\text{KNO}_3/\text{Sulfur}$	333 340 weak	355 (sh) (weak)	400 (sh) (weak)	
<u>Charcoal Black Powder Control</u>				
Maple Charcoal/ $\text{KNO}_3/\text{Sulfur}$	315 332 (moderate)	340 (sh) (moderate)	355 435 (strong)	
<u>Polynuclear Aromatic Compositions</u>				
Anthracene/ $\text{KNO}_3/\text{Sulfur}$		342 354 (moderate)	450 490 (moderate)	
Tetracene/ $\text{KNO}_3/\text{Sulfur}$		350 375 (weak)	475 500 (strong)	
p-Quaterphenyl/ $\text{KNO}_3/\text{Sulfur}$	330 344 (moderate)	375 (sh) (weak)		
Rubrene/ $\text{KNO}_3/\text{Sulfur}$	340 (sh) (weak)	330 378 (weak)		
<u>Compositions containing Hydroquinone and Catechol Moieties</u>				
Hydroquinone/ $\text{KNO}_3/\text{Sulfur}$		346 360 (strong)		Vaporized before Reaction
Hydroquinone/ KNO_3				
Catechol/ $\text{KNO}_3/\text{Sulfur}$	325 340 (strong)			
Catechol/ KNO_3				Vaporized before Reaction

TABLE 3. DSC RESULTS OF PYROTECHNIC MIXTURES (CONTINUED)

<u>System</u>	<u>Low Temperature</u> <u>Exotherm</u>	<u>Moderate Temperature</u> <u>Exotherm</u>	<u>High Temperature</u> <u>Exotherm</u>	<u>Comments</u>
Quinizarin/ KNO_3 /Sulfur	335 345 (moderate)		445 475 (strong)	
Quinizarin/ KNO_3			393 394 (strong)	Sulfur increases exotherm
Leucoquinizarin/ KNO_3 /Sulfur	342 348 (moderate)		440 465 (strong)	Sulfur increases exotherm
Leucoquinizarin/ KNO_3			408 430 (strong)	
Quinalizarin/ KNO_3 /Sulfur		345 360 (moderate)	395 428 (moderate)	Sulfur has little effect
Quinalizarin/ KNO_3			421-422 (strong)	
<u>Compositions Containing Other Phenolic Compounds</u>				
Anthraflavic Acid/ KNO_3 /Sulfur	355 360 (weak)	375 (sh) (weak)	390 420 (strong)	
Anthraflavic Acid/ KNO_3		388-400 (weak)	420-433 (strong)	Sulfur increases exotherm
Phenolphthalein/ KNO_3 /Sulfur			360 450 (strong)	
Phenolphthalein/ KNO_3			482-492 (strong)	Sulfur increases exotherm
Fluorescein/ KNO_3 /Sulfur			360-430 (strong)	

TABLE 3. DSC RESULTS OF PYROTECHNIC MIXTURES (CONTINUED)

<u>System</u>	<u>Low Temperature</u> <u>Exotherm</u>	<u>Moderate Temperature</u> <u>Exotherm</u>	<u>High Temperature</u> <u>Exotherm</u>	<u>Comments</u>
Fluorescein/ KNO_3			387-389 (strong)	Sulfur decreases exotherm
Phenolphthalein/ KNO_3 /Sulfur			360-435 (strong)	
Phenolphthalein/ KNO_3	347-350 (weak)	440-442 (weak)	456-463 (strong)	Sulfur increases exotherm
<u>Compositions Containing Other Classes of Compounds</u>				
Phenolphthalein/ KNO_3 /Sulfur- Disodium Salt	305-335 (moderate)	360(sh) (weak)	380-425 (moderate)	
Phenolphthalein/ KNO_3 Disodium Salt			423-450 (strong)	Sulfur increases exotherm
Fluorescein/ KNO_3 Disodium Salt/ KNO_3 /Sulfur		330-355 (moderate)	385-425 (strong)	
Terephthalic/ KNO_3 /Sulfur Acid		340-345 (strong)	425-460 (strong)	
Terephthalic/ KNO_3 Acid		341-346 (moderate)	437-451 (Strong)	Sulfur decrease exotherm
Anthraquinone		330-340 (weak)	360-370 (weak)	
<u>Organic/KNO_3/Sulfur in proportions 15/75/10 by weight</u>				
<u>Organic/KNO_3 in proportions 25/75 by weight</u>				

REFERENCES

1. James E. Rose, "Investigation on Black Powder and Charcoal," IHTR 433, September 1975, Naval Ordnance Station, Indian Head, MD.
2. K. J. White, H. E. Holmes, and J. R. Kelso, "Effect of Black Powder Combustion on High and Low Pressure Igniter Systems," Proc. of the 16th JANNAF Combustion Meeting, CPIA Publication 308, Vol. 1, pp. 477-497, December 1979.
3. K. J. White, and R. A. Sasse', "Some Combustion and Flamespread Characteristics of Black Powder," Proc. of the 18th JANNAF Combustion Meeting, CPIA Publication 347, Vol. 2, p. 253, October 1981.
4. James E. Rose, "Black Powder - A Modern Commentary," Proc. of the 10th Symposium on Explosives and Pyrotechnics, 6A-1, 1979, Franklin Research Institute, Philadelphia, PA.
5. W. Hintze, Explosivstoffe, Vol. 2, p. 41, 1968.
6. A. D. Kirshenbaum, J. Ballistics, p. 171, July 1978.
7. E. Gray, H. March, and J. Robertson, "The Influence of Charcoal in the Combustion of Black Powder," RARDE, Fort Halstead, Seven Oaks, England. Presented at Basic and Applied Pyrotechnics International Conference, Arcachon, France, October 1982.
8. R. Sasse', "Characterization of Maple Charcoal Used to Make Black Powder," ARBRL-MR-03322 Ballistic Research Laboratory, USA ARRADCOM, Aberdeen Proving Ground, MD, November 1983. (AD-A136-513)
9. E. Ott, H. M. Spurlin, and M. W. Grafflin, High Polymers, Vol. 5, Cellulose and Cellulose Derivatives Part II, p. 514, Interscience Publishers Inc., New York, 1954.
10. R. Sasse', "Strand Burning Rates of Black Powder to One Hundred Atmospheres," Proc. of the 19th JANNAF Combustion Meeting, CPIA Publication 366, Vol. 1, p. 13, October 1982. (AD-A129-087)
11. J. D. Blackwood and F. P. Bowden, Proc. Roy. Soc., London, A 213, 285, 1952.

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